

REPORT DOCUMENTATION PAGE			Form Approved OMB NO: 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 2/24/97	3. REPORT TYPE AND DATES COVERED <i>Technical</i>		
4. TITLE AND SUBTITLE Development and Control of Porosity in Al ₂ O ₃ /AlPO ₄ Coatings		5. FUNDING NUMBERS DAAL03-92-G-0274		
6. AUTHOR(S) Lorraine Falter Francis				
7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES) Department of Chemical Engineering & Materials Science University of Minnesota 421 Washington Ave. S.E. Minneapolis, MN 55455		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		10. SPONSORING / MONITORING AGENCY REPORT NUMBER ARO 29577.6-MS-41P		
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12 b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) This report describes a new method for low temperature preparation of porous ceramic coatings. A reaction between aluminum oxide and phosphoric acid is used to bind particles together and control porosity. Porous ceramic coatings with pore contents ranging from 25 to 50% were prepared at processing temperatures as low as 300°C. The porosity in coatings prepared from dispersions containing alumina and phosphoric acid was controlled by the relative amount of acid and hence relative amount of aluminum phosphate reaction product. The addition of aluminum chloride to the dispersion led the formation of fine aluminum hydroxide precipitates which react with phosphoric acid at lower temperatures to form aluminum phosphate; these fine reaction products help to bind the alumina particles together without affecting the pore content. The success of this low-temperature phosphate route leads to the possibility of other coating systems which use chemical reactions to promote bonding and control porosity.				
14. SUBJECT TERMS Ceramic Coatings, Porosity, Al ₂ O ₃ , AlPO ₄		15. NUMBER OF PAGES 8		
		16. PRICE CODE		
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

DTIC QUALITY INSPECTED 2

19970321 026

DEVELOPMENT AND CONTROL OF POROSITY IN $\text{Al}_2\text{O}_3/\text{AlPO}_4$ COATINGS

TECHNICAL REPORT

LORRAINE FALTER FRANCIS

24 FEBRUARY 1997

U. S. ARMY RESEARCH OFFICE

CONTRACT GRANT NUMBER DAA3-92-G-0274

UNIVERSITY OF MINNESOTA

APPROVED FOR PUBLIC RELEASE:
DISTRIBUTION UNLIMITED

THE VIEWS, OPINIONS, AND/OR FINDINGS CONTAINED IN THIS REPORT ARE THOSE OF THE AUTHOR AND SHOULD NOT BE CONSIDERED AS AN OFFICIAL DEPARTMENT OF THE ARMY POSITION, POLICY, OR DECISION, UNLESS SO DESIGNATED BY OTHER DOCUMENTATION.

STATEMENT OF PROBLEM STUDIED

The processing of ceramic coatings with controlled porosity is needed for a variety of applications, including chemical sensors, membranes, and applications that require controlled optical and dielectric properties. In this research, porosity control was approached by a unique low temperature processing route. Alumina particles were fabricated into a porous coating and the amount of aluminum phosphate reaction product controlled the porosity and mechanical properties. The research was motivated by both the exploration of a general method of porosity control and the need for a robust porous coating to act as a matrix in an interpenetrating ceramic composite coating (the subject of an ARO ASSERT grant.)

The technology for bonding the alumina particles in the coating falls into the general category of chemically bonded ceramics (CBC's)¹⁻⁹. Examples of CBC's include mortars, cements and concretes. CBC's have the advantage of developing strength at low processing temperatures, with some even showing remarkable properties with room temperature processing or curing⁴. Most CBC's are prepared by one of three routes: (i) hydration (e.g., portland cements, calcium hydroxide/oxide cements), (ii) precipitation reactions (e.g., ion exchange materials), and (iii) acid/base reactions (e.g., phosphates, certain oxides)³. A reaction of the last variety was used in this research. The reaction between alumina powder and phosphoric acid (H_3PO_4) at temperatures below 300°C forms aluminum phosphate⁶. The alumina/aluminum phosphate system has been used as a cement binder, but until now has not been applied to the fabrication of coatings.

SUMMARY OF MAIN RESULTS

Processing and Characterization:

Coatings were prepared by depositing an aqueous dispersion of alumina particles containing phosphoric acid and sometimes aluminum chloride. The alumina particles had an average diameter of $0.3\ \mu\text{m}$ (AL-16SG, Alcoa). Dispersions were prepared by adding phosphoric acid solution (85 wt%) into an aqueous dispersion of alumina (44.4 wt% alumina with $0.001\ \text{g/cm}^3$ citric acid). The amount of phosphoric acid solution added was varied to provide dispersions with $\text{H}_3\text{PO}_4 : \text{Al}_2\text{O}_3$ weight ratios of 0.0106:1 to 0.106:1. Another set of dispersions was prepared with a $\text{H}_3\text{PO}_4 : \text{Al}_2\text{O}_3$ weight ratio of 0.106:1 and with aluminum

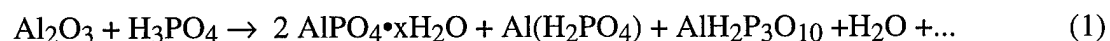
chloride added in an amount ranging from 0.001:1 to 0.1:1 ($\text{AlCl}_3:\text{Al}_2\text{O}_3$ by weight). For these dispersions, the aluminum chloride was added to the aqueous alumina dispersion (44.4 wt%) before the addition of phosphoric acid solution. Since HCl vapor was generated in the process of adding aluminum chloride to water, the procedure was carried out in a hood. The dispersions were coated onto glass and other substrates using a fixed gap draw-down blade. Coatings were dried in air overnight and then heated at either 100°C (24-48 hours), 300°C (2 - 4 hours), or 500°C (2 hours). Coatings were typically 30 μm thick, but could be prepared with a wide range of thicknesses.

The reactions involved in the chemical bonding and the resultant reaction products were analyzed using thermal analysis methods and x-ray diffraction. Thermogravimetric analysis (TGA, Perkin-Elmer TGA7) and differential thermal analysis (DTA, Perkin-Elmer DTA1700) were carried out on coatings removed from their substrates. The crystalline phases present in the coatings were analyzed by X-ray diffraction (XRD, Seimens D-50).

The microstructure of the ceramic coatings was characterized by field emission scanning electron microscopy (FEG-SEM, Hitachi S-800). Cross-sectional and plan views of the coating microstructures were viewed. Coating porosity was measured using a thermogravimetric volatilization of liquids technique (TVL) method¹⁰.

Results

The composition of the coating dispersion as well as the thermal treatment controlled the ceramic phase connectivity, coating porosity and coating strength. Two systems were investigated: (i) alumina with phosphoric acid and (ii) alumina with aluminum chloride and phosphoric acid. For both systems, reactions ensue and affect the phase composition as well as the microstructure of the coating. For coatings prepared with alumina and phosphoric acid, alumina reacts with phosphoric acid according to^{6,11-12}:



This reaction is unbalanced as several reaction products are possible, depending on the thermal conditions. Reaction with phosphoric acid will occur in the dispersion, but is more likely when the coating is dried and heated. Also on heating, the aluminum phosphate reaction product,

originally amorphous, crystallizes. For coatings prepared with aluminum chloride, a reaction takes place when the aluminum chloride is added to the aqueous alumina dispersion:



The Al(OH)_3 generated can then react when phosphoric acid is added⁹:



Compared with reaction (1), reaction (3) takes place much more readily at room temperature. Based on these reactions, the coating dispersion composition (acid content, presence and amount of aluminum chloride) and the heating temperature were the main variables affecting the microstructure. All coating dispersions were well stabilized; hence, the effect of alumina particle agglomeration differences on microstructure was not important.

The phosphoric acid content controlled the porosity and microstructural features in coatings prepared with alumina and phosphoric acid. Increasing the acid content from 0.0106:1 to 0.106:1 ($\text{H}_3\text{PO}_4:\text{Al}_2\text{O}_3$ by weight) led to rounding of the alumina particles and the formation of greater amounts of aluminum phosphate as "bridges" between particles. Figure 1 compares the microstructure of coatings with high and low acid loadings. The presence of aluminum phosphate on the surfaces of alumina particles and between them was also verified by preliminary TEM studies (not shown). A similar, but less dramatic change in microstructure, was observed in coatings of this type with an increase in temperature for coatings of a given phosphoric acid content. Porosity also varied with acid content. Figure 2 shows the decrease in porosity from 50 to 30 vol% with increased acid loading. Average pore size was observed by SEM to decrease as well.

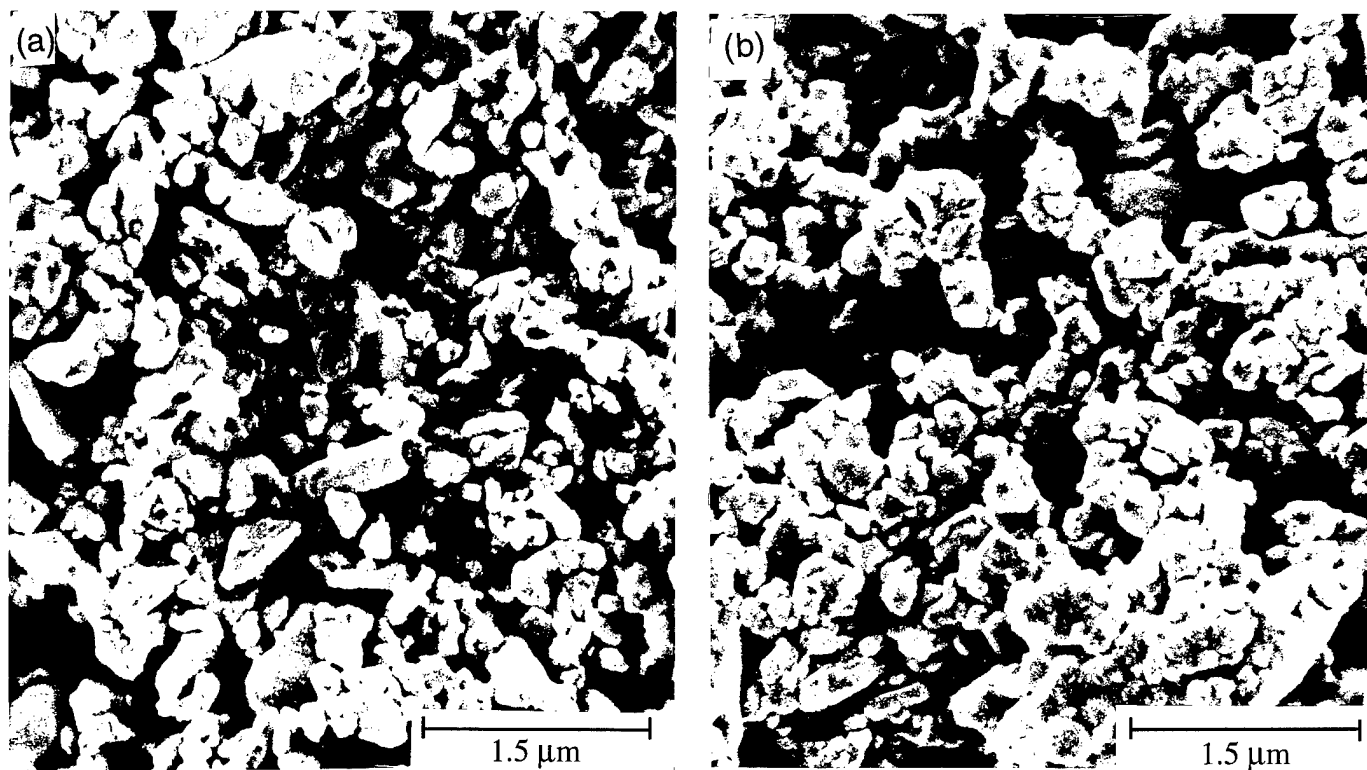


Figure 1 SEM photomicrographs of coatings prepared with H_3PO_4 : Al_2O_3 weight ratios of (a) 0.005:1 and (b) 0.05:1. Coatings were heated at 300°C.

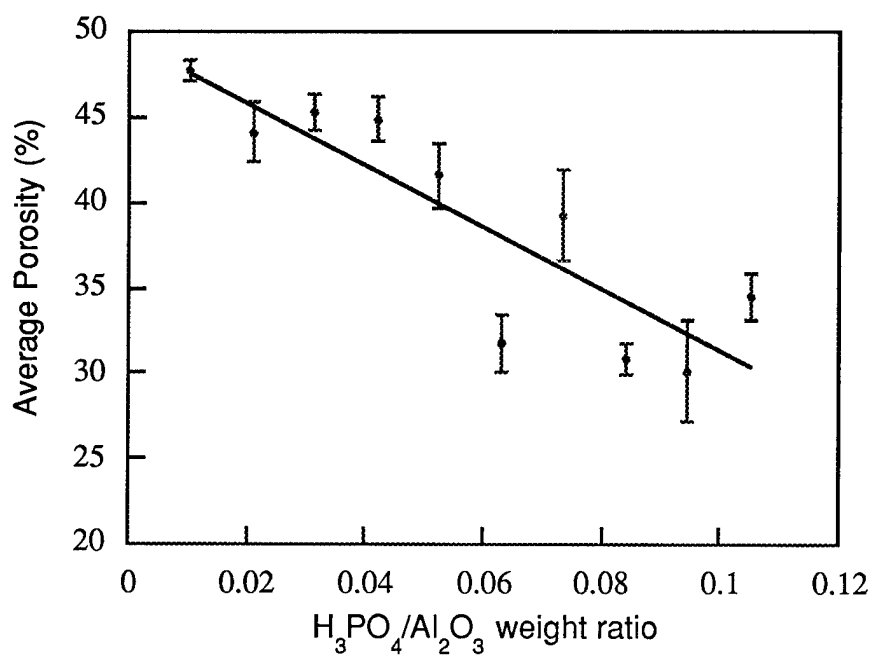


Figure 2 Effect of phosphoric acid content on coating porosity. Coatings were prepared from dispersions of alumina and phosphoric acid and heated to 300°C.

The addition of aluminum chloride to the coating system with the highest acid loading (0.106:1) did not change the microstructure significantly. SEM photomicrographs of coatings prepared with a range of AlCl_3 additions had similar features as those shown in Figure 1, but these features (rounded particles, bridges between particles) developed at lower temperature. Porosity measurements revealed that the pore content of the coating was invariant to the aluminum chloride addition. This difference is discussed in the next section.

Figure 3 shows DTA data for coatings prepared with and without AlCl_3 . A single endotherm, presumably from water removal (based on TGA data), was evident for the sample with AlCl_3 , while the coating prepared with alumina and phosphoric acid showed an additional endotherm at 220°C . This second endotherm indicates that further reaction occurs in these coatings, while reaction is complete at lower temperatures when aluminum chloride is used.

Analysis of the crystalline phase content of the coatings revealed the relative amount of crystalline aluminum phosphate which forms in the coatings. In coatings prepared from aqueous dispersions of alumina and phosphoric acid, crystalline AlPO_4 was not observed with

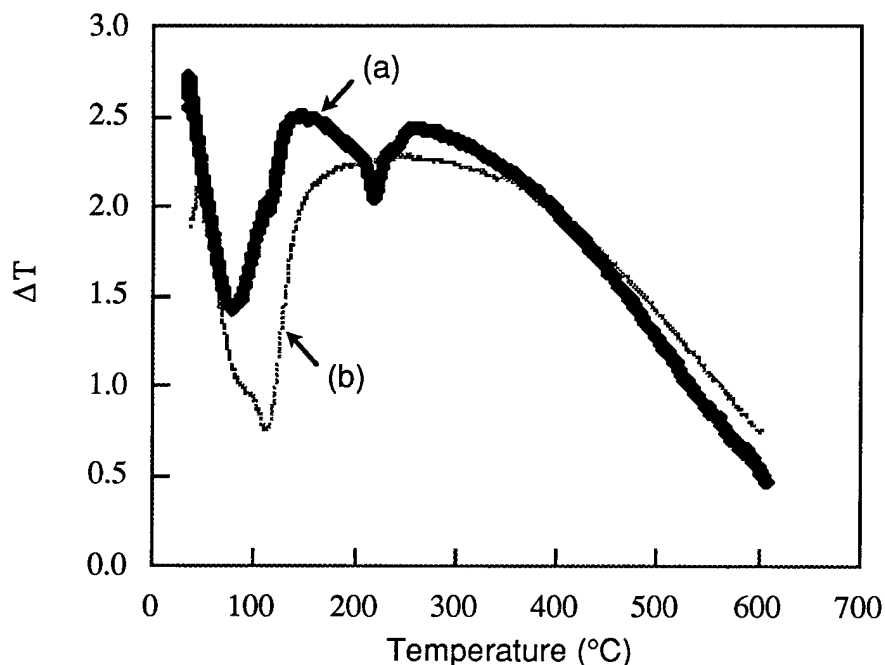


Figure 3 DTA data for (a) coatings prepared with alumina and phosphoric acid (0.064:1, $\text{H}_3\text{PO}_4:\text{Al}_2\text{O}_3$ weight ratio) and (b) coatings prepared with alumina, aluminum chloride and phosphoric acid (0.106:1, $\text{H}_3\text{PO}_4:\text{Al}_2\text{O}_3$ and 0.1:1 $\text{AlCl}_3:\text{Al}_2\text{O}_3$).

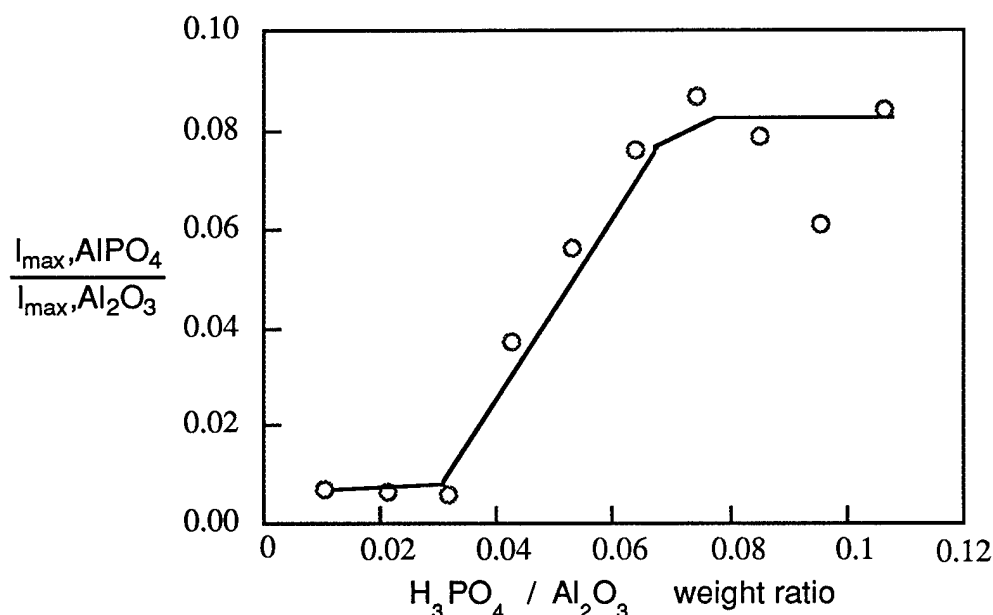


Figure 4 Effect of phosphoric acid loading on the relative amount of crystalline AlPO_4 in coatings heated at 500°C for 2 hours.

thermal treatments at or below 300°C , even when the highest phosphoric acid content used. Coatings heated to 500°C had a low intensity aluminum phosphate peak when the acid loading surpassed 0.05:1 ($\text{H}_3\text{PO}_4:\text{Al}_2\text{O}_3$ by weight). The phosphate phase in coatings with a lower acid loading could have been crystalline at an amount below the detection limit of XRD. The relative intensity of the most intense peak for AlPO_4 increased with acid loading, but then leveled off at higher loadings (See Fig. 4). This trend indicates that the extent of reaction between phosphoric acid and alumina may be limited by diffusion through the aluminum phosphate product layer. For coatings prepared with aluminum chloride, there was no evidence of crystalline AlPO_4 .

Coating Microstructure Development

The control of the porous microstructure of coatings prepared with alumina and phosphoric acid can be understood in terms of the reactions. During coating and drying, a layer of phosphoric acid deposits on the alumina particles. On heating, phosphoric acid reacts at the alumina particle surfaces to form a layer of hydrated aluminum phosphate. Further reaction requires diffusion of reactant through the product layer; if this layer is dense, then the extent of reaction will increase with $(\text{time})^{1/2}$ and will depend on the diffusion coefficients of the reactants

and, hence, the temperature. XRD results support this hypothesis. The formation of an aluminum phosphate layer on the particles has the effect of joining the particles together; SEM observations indicate that particle-particle contacts are not simple point contacts that are typically found in alumina coatings without phosphoric acid. The effect of acid loading on porosity can be understood considering the density difference between aluminum phosphate and alumina (2.56 g/cm^3 vs. 3.98 g/cm^3 , respectively). For a given temperature, coatings with larger acid loadings form more aluminum phosphate and have less open porosity per unit volume (i.e., the conversion of a high density solid to a low density solid consumes pore space). These coatings are also more robust due to their greater connectivity. Temperature also plays an important role in microstructural development. As temperature is increased, diffusion through the phosphate layer is facilitated, allowing further reaction and the formation of more phosphate and a decrease in porosity. Also, as the temperature is increased, the $\text{AlPO}_4 \cdot x \text{H}_2\text{O}$ loses water and there may be some sintering, leading to shrinkage of the coating.

Coatings formed from dispersions containing aluminum chloride do not show a drop in porosity with increasing phosphate content. In the preparation of the coating dispersion, aluminum chloride reacts with water in the alumina dispersion to form aluminum hydroxide particles; these fine particles react with phosphoric acid when it is added to the dispersion. The result is formation of aluminum phosphates in the dispersion before coating deposition and less conversion of the alumina particles to phosphate in the solid coating. The coating after drying is comprised of alumina, aluminum phosphate reaction products, phosphoric acid and any remaining aluminum hydroxide. While some phosphoric acid is consumed by reaction with aluminum hydroxide, at least half remains. As the aluminum chloride concentration grows from 0.001:1 to 0.1:1 ($\text{AlCl}_3:\text{Al}_2\text{O}_3$ by weight), the amount of residual phosphoric acid (assuming complete reaction with aluminum hydroxide) drops from 0.098:1 to 0.033:1 ($\text{H}_3\text{PO}_4:\text{Al}_2\text{O}_3$ by weight). On heating, there is the possibility of additional reaction between phosphoric acid and alumina (and residual aluminum hydroxide). Conversion of aluminum hydroxide to aluminum phosphate does not involve a significant density change and will not affect the porosity. There may also be a tendency for the aluminum hydroxide particles and aluminum phosphate reaction products to form on alumina surfaces in the suspension and during drying; the presence of this surface layer would present a barrier to further reaction between residual phosphoric acid and alumina and account for the observed constant porosity with aluminum chloride content.

Summary

Porous ceramic coatings with pore contents ranging from 25 to 50% were prepared at processing temperatures as low as 300°C. The porosity in coatings prepared from dispersions containing alumina and phosphoric acid was controlled by the relative amount of acid and hence relative amount of aluminum phosphate. The addition of aluminum chloride to the dispersion led the formation of fine aluminum hydroxide precipitates that react with phosphoric acid at lower temperatures to form aluminum phosphate reaction products; these fine reaction products help to bind the alumina particles together without affecting the pore content. The success of this low-temperature phosphate route leads to the possibility of other coating systems which use chemical reactions to promote bonding and control porosity.

References

1. Popovics, S., Rajeendran, N., and Penko, M, "Rapid Hardening Cements for Repair of Concrete," *ACI Materials Journal*, Jan-Feb (1987) p. 64-73
2. Johnson, B.R., Gulgun, M.A., and Kriven, W.M. "Chemically Bonded Ceramic Matrix Composites: Densification and Conversion to Diffusion Bonding," *Mat. Res. Soc. Symp. Proc.* **365** (1995) p. 67-72.
3. Sarkar, A.K., "Phosphate Cement-Based Fast-Setting Binders," *Ceramic Bulletin*, **69** [2] (1990) p. 234-238
4. Gulgun, M.A., Johnson, B.R., Kriven, W.M., "Chemically Bonded Ceramics as an Alternative to High Temperature Composite Processing", *Mat. Res. Soc. Symp. Proc.* **346** (1994) p. 511-516.
5. Wygant, J.F., "Cementitious Bonding in Ceramic Fabrication," p. 171-188 in *Ceramic Fabrication Processes*, Ed. W.D. Kingery (Technology Press of MIT, Cambridge, 1958).
6. Gonzalez, F.J., and Halloran, J.W., "Reaction of Orthophosphoric Acid with Several forms of Aluminum Oxide," *Ceramic Bulletin*, **59** [7] (1980) p. 727-738.
7. Semler, C.E., "A Quick-Setting Wollastonite Phosphate Cement," *Ceramic Bulletin*, **55** [11] (1976) p. 983-988.
8. Roy, D.M., "New Strong Cement Materials: Chemically Bonded Ceramics", *U.S. Woman Engineer*, March/April (1988) p. 32-38
9. Lyons, J.W., McEwan, G.J., and Siebentha, "Phosphoric Acid in Solution: Stailization: II," Natl. Acad. Sci-Natl. Res. Council Publ. No. 964 (1962) p. 5-24.
10. Craig, B.D., Francis, L.F., and Abrams, L. "Measurement of Porosity in Ceramic Coatings by Thermogravimetric Volatilization of Liquids", *J. Am. Ceram. Soc.*, **79**[12] (1996) p. 3317-20.
11. Greger, H.H., *Brick and Clay Record*, 1950 , V 117, 63
12. Greger, H.H., U.S.P. 2460344; B.P. 597169